LITHIUM INCORPORATED PLASTICIZED MEMBRANES BASED ON ECO-FRIENDLY POLYMERS FOR SUPERCAPACITOR APPLICATIONS

A SYNOPSIS

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M NANDHINILAKSHMI

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ANAND NAGAR, KRISHNANKOIL – 626 126

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1. Introduction

Over the past few decades, there has been a significant shift in research focus towards the exploitation and utilization of renewable energy sources, such as wind energy, tidal energy, and solar energy. This change has been driven by increasing consumption and the rapid depletion of fossil fuels, which have traditionally accounted for the majority of global electricity generation. To ensure the widespread usage of renewable energies, efficient energy storage and conversion technologies have become crucial. One important application of these technologies is focused in the development of portable electric devices and hybrid electric vehicles, which cater to the needs of our mobile society. In line with this trend, various electrochemical systems have been designed and developed using advanced energy conversion and storage mechanisms. These include lithium-ion batteries, electrochemical capacitors (also known as electrochemical supercapacitors), fuel cells, and metal-air batteries[1]. Supercapacitors are the devices that have determined their energy density and power density levels in between the performances of capacitors and battery. Few ultracapacitors are already placed in the market, but, tuning of polymer-based supercapacitors is yet to establish their leading role in providing efficient devices[2].

The fundamental elements of supercapacitors (SC) are known as electrode and, electrolyte/separator**.** A SC is made up of two porous electrodes, with an electrolyte sandwiched between them. The electrolyte materials should have high ionic conductivity, a promising electrochemical window, and strong thermal and mechanical stability. The energy in SC is stored by charge separation in Helmholtz double layers across the blocking electrode-electrolyte interfaces as a result of electrostatic interactions between the ions in the electrolyte and the active electrode materials. SC is more environmentally friendly than batteries because of its higher power density, longer lifespan and higher cyclic ability[3]. SC utilizes solid polymer electrolyte (SPE) membranes that provide several advantages, including a broad operational temperature range, minimal volatility, impressive energy density, and negligible vapor pressure. These membranes have thin and flexible polymeric structure which enables the fabrication of SC in a variety of forms, including solid, flexible, and even bending structures[4].

Environmental considerations influence the selection of biopolymers. Bio-polymers are derived from renewable sources found in nature. These bio-polymer electrolytes are not only cost-effective but also environmentally friendly. These advantages have made bio-polymer electrolytes a promising alternative to synthetic polymers in electrochemical applications. Researchers have suggested using natural biopolymers like chitin, starch, pectin, carrageenan, agar-agar, methylcellulose, cellulose acetate, etc. to develop solid biopolymer electrolytes (SBE) as a solution to address the pollutants. Various synthesis techniques, including polymer gel, composite and plasticized blending are employed by researchers to enhance the properties of polymers. Among the various approaches, polymer blending is one of the most feasible techniques to synthesis solid polymer electrolyte. Polymer blending improves the electrochemical performances of electrolytes by (1) enhancing the functional groups of the systems (2) enhancing the mechanical integrity of the system (3) decreasing the T_g of the systems (4) boosting the amorphous contents of the system (5) improving the interface between the electrodes/electrolytes (6) reducing the activation energy (7) reducing the bulk and interface resistance and (8) improve the physical properties.

Further improve the free space in the electrolyte, researchers have explored several strategies to enable room-temperature operation in devices, and another one approach involves using plasticized polymer-salt complexes. These complexes incorporate low-molecular-weight liquid plasticizers such as polyethylene glycol, ethylene glycol, and glycerin. The primary goal of adding these plasticizers is to enhance the segmental motion and flexibility of the polymer chains. The addition of plasticizers to the polymeric system enhances its ionic conductivity.

The presence of liquid plasticizers in the system also has other benefits. This reduces the degree of crystallinity of the material and promotes ion dissociation of salts. This improves ionic transport within the system by increasing the concentration and mobility of charge carriers. This is crucial for the mechanical strength, and thermal stability for efficient function of electrochemical devices, as it enables the rapid transport of ions between the anode and cathode, resulting in improved device performance.

Alkali metal salts are commonly added to achieve good conduction (including lithium salts). However, lithium-based ionic salts are most popular because lithium ions

(Li^+) are smaller in size, which leads to a high gravimetric Coulombic density. Li^+ ion incorporation with the polar group of the blend polymer is made possible by feeble coordination in the presence of lithium salt ($LiNO_3$, LiI, $LiCF_3SO_3$, and $LiClO_4$) and increases the charge carriers and thereby rises the ionic conduction. The goal of this research is to prepare lithium ion based plasticized biopolymer blend electrolyte.

2. Literature Review

Algae, which are photosynthetic organisms, have a taxonomy that is complex and subject to debate. They can be classified into two main types: microalgae and macroalgae (seaweeds). Microalgae are small-sized algae found in various environments such as benthic, littoral and throughout marine waters as phytoplankton. On the other hand, macroalgae or seaweeds are larger and commonly occupy the littoral zone. Seaweeds are multicellular photosynthetic microorganisms that hold significant potential as a biomass resource for the production of valuable biochemical products and biofuels, either completely or partially replacing terrestrial biomass[5].

Especially seaweeds exhibit specific characteristics that make them excellent candidates for renewable sources. For instance, seaweed algae possess abundant cell wall polysaccharides, storage polysaccharides, and mycopolysaccharides. These polysaccharides are chosen to prepare as solid electrolyte due to their sustainable and abundant availability, as well as their unique chemical composition not found in other organisms. Algal polysaccharides form a diverse class of biopolymers derived from different types of seaweeds. Green seaweeds, such as ulvans, brown seaweeds, such as alginates, and red seaweeds, such as carrageenan, are examples of sources for these polysaccharides. The characteristics and conclusions of research publications on carrageenan-based polymer electrolytes are discussed below[6].

Rudhziah et al[7]. developed a solid electrolyte utilizing kappa-carrageenan, a type of biopolymer with ammonium nitrate using a solvent consisting of 1% acetic acid. These electrolytes demonstrated remarkable ionic conductivity as 1.41×10^{-4} S cm^{-1}, and exhibited a minimum activation energy of 0.06eV.

Nithya et al[8] also published a report on an electrolyte that was developed using kappa-carrageenan biopolymer with 200 mg of NH_4Cl. The electrolytes demonstrated remarkable properties, including a high ionic conductivity measured as 2.99×10^{-4} S

cm^{-1}, and a minimum activation energy of 0.02eV. An electrochemical cell was fabricated using the electrolyte. The open-circuit voltage (OCV) of the cell was determined to be 1.74 V.

Arof et al[9]. developed an electrolyte by a blended film of chitosan and iota (ι)-carrageenan. The film was doped with orthophosphoric acid (H_3PO_4) as an ionic dopant and poly (ethylene glycol) (PEG) as a plasticizer. This electrolyte was prepared using a solution-casting method. The researchers achieved a maximum conductivity value of 6.29×10^{-4} S cm^{-1}. Additionally, the specific discharge capacitance of the Electrochemical Double Layer Capacitor was found to be 35 F g^{-1} at a current drain of 0.11mA cm^{-2}. Notably, this specific discharge capacitance remains constant over the course of 30 cycles.

An electrolyte prepared by Zainuddin et al[10], through a solution-casting method using carboxymethyl cellulose (CMC), kappa carrageenan and NH_4NO_3.This electrolyte achieved a maximum conductivity of 2.00×10^{-4} S cm^{-1} and utilized for the fabrication of supercapacitor which exhibits stable performance for 10,000 cycles. The average specific capacitance (Cs) measured as 20 Fg^{-1} and 25 Fg^{-1}, respectively through charge-discharge and cyclic voltammetry analysis.

Tingting Ye et al[11], reported the solid-state supercapacitor fabricated by poly(vinyl alcohol) (PVA) blended with carrageenan (car) gel polymer electrolyte and activated carbon as electrodes which showcased several desirable attributes. The maximum conductivity of 3.47×10^{-4} S cm^{-1} was attained. It had a high specific capacitance of 406 mF cm^{-2} at 5 mA cm^{-2}, indicating its ability to store a substantial amount of electrical charge per unit area. Furthermore, the supercapacitor demonstrated excellent rate performance, retaining 99.9% of its capacitance after 5500 cycles.

The films which are synthesized by blending chitosan and κ-carrageenan by Shuhami et al[12]. reported its conductivity at room temperature. It was observed that the conductivity of the film consisting of 0.5 g of chitosan + 0.5 g of κ-carrageenan was measured to be $(1.38 \pm 0.36) \times 10^{-6}$ S cm^{-1}, while the film containing 0.5 g of chitosan + 0.5 g of κ-carrageenan + 0.1765 g of ammonium nitrate presented a conductivity of $(2.39 \pm 0.83) \times 10^{-4}$ S cm^{-1}. Moreover, the electrochemical double-layer capacitor (EDLC) utilizing the combined electrolyte demonstrated an average discharge

capacitance ranging from 13 to 18.5 F g^{-1}.

The research report on carrageenan with salt complex electrolyte primarily focuses on its application in batteries. The study aims to investigate the potential of using carrageenan as a base material for polymer electrolyte membranes in order to enhance conductivity for electrochemical devices.

The natural gums and resins obtained from different tree species have revealed their potential for creating bio-based electrolytes. Gums can be classified based on their source of extraction, chemical structure, and physical characteristics. Several types of gums are such as Acacia gum, AG, Guar gum, Tragacanth gum, Gellan gum, Moringa gum, and Xanthan gum. The hydroxyl groups in the gum, combined with their hydrophilic nature and contributed to the modulation of viscosity and gelling properties when incorporated into different substances[13,14].

Shilpa et.al [15] conducted a research on a blend polymer electrolyte system for lithium-ion batteries. The blend system prepared by pectin and guar gum: both are formed as biopolymers. They are also added with lithium salt (LiTFSI) to enhance conductivity. Through XRD and FTIR analysis, the researchers confirmed the phase identification of the blend and the polymer complex. The conductance spectra results reveals that the blend polymer electrolytes exhibits a conductivity of 1.59×10^{-4} Scm^{-1} at atmospheric temperature.

Pawlicka et al. [16] developed a blend polymer electrolyte using Xanthan gum (XG) and polyvinylpyrrolidone (PVP) through the casting method. They found that the sample containing 2.00 g of acetic acid exhibited the highest conductivity value of 7.26×10^{-5} Scm^{-1}.

Cholant et al.[17] conducted a study on solid polymer electrolytes (SPEs) using poly(vinyl alcohol) (PVA), gum arabic (GA), and $LiClO_4$. In their report, the highest ionic conductivity achieved as 1.6×10^{-4} Scm^{-1} at 25 °C and 8.6×10^{-4} Scm^{-1} at 80 °C. These membranes also exhibited good transparency, ranging from 80% to 87% in the 400 nm and 633 nm wavelengths. Furthermore, they demonstrated thermal stability up to 150 °C.

Cholant et al.[18] reported a solid polymer electrolyte (SPE) by a combination of poly(vinyl alcohol) (PVA) and gum arabic (GA) with varying amounts of acetic acid. In their study, they reported that the highest ionic conductivities of 2.22×10^{-5} Scm^{-1} at 25 °C and 17.70×10^{-5} Scm^{-1} at 80 °C were achieved for the PVA/GA blend containing 42 wt.% of acetic acid.

The study conducted by Asnawi et al.[19] involved on preparation of polymer electrolyte system using chitosan/dextran-NaTf with various glycerol concentrations. The most conductive plasticized electrolyte exhibited a DC ionic conductivity of 6.10×10^{-5} Scm^{-1}. Additionally, they identified that the transference numbers of ion (t_{ion}) and electron (t_e) for this electrolyte as 0.988 and 0.012 respectively. Furthermore, the breakdown voltage of the electrolyte was noted to be 2.55 V from the LSV analysis. These characters made the electrolyte as a suitable one for potential application in electrochemical energy devices.

The study by Shukur et al.[20] investigated the impact of plasticization on the electrical conductivity and dielectric properties of starch-chitosan blend biopolymer electrolytes. In the unplasticized system, the highest conductivity at room temperature is measured at $(9.72\pm0.95)\times10^{-5}$ Scm^{-1}, whereas in the plasticized system, the highest conductivity is significantly higher as $(1.44\pm0.51)\times10^{-3}$ Scm^{-1}. Additionally, the plots illustrating the relationship between dielectric constant (ε_r) and frequency for both plasticized and unplasticized systems exhibit non-Debye behavior.

Venkatesh et al.[21] prepared natural polymer electrolytes using guar gum, sodium nitrate, and propylene carbonate. The addition of salt results in an achieved ionic conductivity value of 2.43×10^{-7} Scm^{-1}, which was further enhanced to 2.96×10^{-4} Scm^{-1} with the introduction of plasticizer. The variation of conductivity with temperature obeys the thermally activated Arrhenius type behavior. Additionally, dielectric analysis was exhibited by non-Debye behavior. The majority charge carriers were predominantly ions based on the transference number measurement.

Lithium-based salts play a crucial role in the development and enhancement of solid polymer electrolytes (SPEs) in various electrochemical devices, such as lithium-ion batteries, lithium ion capacitor, etc. The advantages of using lithium-based salts in

SPEs are numerous and contribute significantly to the overall performance and efficiency of these devices.

Fuzlin et al.[22] conducted a study focusing on biopolymer electrolytes (BEs) blended with alginate and $LiNO_3$. Through the FTIR analysis, they observed complexation taking place as a result of the incorporation of $LiNO_3$ via the COO^- group of alginates. The interaction between alginate and $LiNO_3$ resulted in an enhanced ionic conductivity of the BEs, increasing from 3.24×10^{-7} Scm^{-1} for the salt undoped sample and a highest value of 1.14×10^{-4} Scm^{-1} for the sample containing 15 wt. % $LiNO_3$. Moreover, the dielectric behavior of the BEs system was characterized using complex permittivity and electrical modulus, revealing non-Debye behavior.

Khanmirzaei et al.[23] carried out a study on biodegradable polymer electrolyte systems, specifically focusing on Rice Starch-Lithium Iodide (RS-LiI) films. These films were prepared through the solution casting method. It was found that, a RS:LiI film with a ratio of 65 wt.%:35 wt.% exhibited the highest ionic conductivity, measuring at 4.68×10^{-5} Scm^{-1} at ambient temperature. The study includes an analysis of the temperature-dependence of ionic conductivity, which was found to follow the Arrhenius model. Based on the related plot, the activation energy for the highest conducting composition was determined to be 0.41 eV.

Nadirah et al.[24] conducted a study on nanocomposite solid biopolymer electrolyte, which involved preparing a material composed of corn starch (CS) and lithium iodide (LiI) with varying concentrations of nanosize aluminium oxide (Al_2O_3) using the standard solution casting technique. By incorporating 2 wt. % Al_2O_3 into CS-LiI, they achieved a maximum room temperature ionic conductivity of $(6.73 \pm 0.78)\times10^{-4}$ Scm^{-1}. Furthermore, thermal analysis using DSC revealed that the best conducting film exhibited the lowest T_g and T_m, indicating improved segmental motion for ion migration.

The study by Lotebulo Ndruru et al.[25] focused on creating Biopolymer electrolyte (BPE) membranes using a simple solution casting technique. The membranes were made by incorporating different weight percentages of LiClO4, ranging from 0% to 20% (w/w). The most successful result was achieved with 10%

(w/w) $LiClO_4$-complexed methyl cellulose, which exhibited an ionic conductivity of 3.66×10^{-5} Scm^{-1}, a tensile strength of 35.97 MPa, and a thermal stability between 208.4 to 338.2°C. These properties meet the minimum standard for applicable in Li-ion batteries. However, further enhancement of the ionic conductivity could be achieved by incorporating a plasticizer or ionic liquid.

The study by Leo Edward et al.[26] focused on solid polymer electrolyte, which is made by solution casting and the polymer is composed of a mixture of chitosan and agar-agar, plasticized with polyethylene glycol (PEG) as the host polymer and lithium perchlorate ($LiClO_4$) as a dopant. The blend polymer electrolyte consisting of 75% (CS, AA), 15% PEG, and 10% $LiClO_4$ had a maximum ionic conductivity of 4.6×10^{-4} Scm^{-1} at ambient temperature. The higher conducting sample's electrochemical stability window was stable up to 3.3 V as determined by linear sweep voltammetry.

Majumdar et al.[27] have reported on the development of environmentally friendly solid biopolymer electrolytes (SBE) utilizing chitosan acetate (CA) and lithium perchlorate ($LiClO_4$). At 300 K, the addition of $LiClO_4$ salt increases the ionic conductivity of chitosan acetate from around 10^{-9} Scm^{-1} to approximately 10^{-5} Scm^{-1}. At ambient temperature and a concentration of 44.44 wt.% $LiClO_4$ added SBE exhibits the maximum ionic conductivity of 1.33×10^{-5} Scm^{-1}.

Shaffie et al.[28] conducted a research on a biopolymer electrolyte system made of Chitosan-Starch blend doped with varying amounts of $BMIMNO_3$ (2-aminothiophenols with 2-bromoalkanoates) using the solution casting technique. The crystalline structure of the system was determined by analyzing data obtained from X-ray diffraction (XRD). The findings demonstrated the benefits of an ionic liquid as a charge carrier and highlighted that the inclusion of 5% $BMIMNO_3$ results in the highest conductivity of $(2.26\pm0.96) \times 10^{-4}$ Scm^{-1}. Furthermore, the conductivity temperature relationship suggested that the system follows the Vogel-Tamman-Fulcher (VTF) behavior.

Nur Umira Taib et.al. reports[29] on the solution casting method used to prepare solid polymer electrolytes. The electrolyte is made up of chitosan, succinonitrile (SN) as a plastic crystal, and lithium bis (trifluoromethyl sulfonyl) imide (LiTFSI) as a salt. With the addition of LiTFSI and SN, XRD measurements verified the amorphous nature

of the polymer electrolyte sheets. At room temperature, the films had a steady and maximal ionic conductivity of 4.00×10^{-4} Scm^{-1}.

Sampath Kumar et.al.[30] deals with the bioactive polymer electrolyte based on tamarind seed polysaccharide (TSP) as the host polymer and incorporating different concentrations of Lithium triflate ($LiCF_3SO_3$) as the ionic dopant salt through a solution-casting technique. The optimum conducting sample, with a ratio of 1 g TSP to 0.45 g $LiCF_3SO_3$, exhibited a conductivity value of 8.37×10^{-4} Scm^{-1}. Additionally, a lithium ion conducting battery was constructed, and the open circuit voltage (OCV) of the cell was measured to be 1.85 V for the most conductive polymer electrolyte (1 g TSP: 0.45 g $LiCF_3SO_3$).

3. Objectives

The objectives of present research work are,

- The main objective of this work is to prepare environment friendly electrolytes based on biopolymers
- To select biopolymers to prepare biopolymer electrolytes
- To prepare pure iota carrageenan (host polymer) film through simple solution casting technique.
- To prevent fungal properties in the host polymer, another gum-based polymer acacia gum is blended with the host polymer.
- To increase the conductivity of the blend, various amount of plasticizer ethylene glycol is added
- To improve the efficiency of the device made by polymer electrolytes, lithium based salts ($LiNO_3$, LiI, $LiCF_3SO_3$ and $LiClO_4$) are used as the ion source with the optimized plasticized blend ratio.
- The Prepared electrolytes are characterized by XRD, FTIR, AC Impedance analysis and Ion transport analysis.
- The higher conductivity electrolyte is used for the fabrication of symmetrical capacitors using activated carbon as electrode material.
- The electrochemical properties of the symmetrical capacitor are analyzed from cyclic voltammetry and Galvanostatic charge-discharge.

4. Research Problem

Polymer electrolytes (PEs) play a crucial role in manufacturing high-performance energy storage devices. These materials fall into two main categories: synthetic polymers and natural polymers. The synthetic polymers contribute to environmental pollution due to their non-biodegradability. So, the researcher's focus turns into biopolymers. Over the years, various bio-polymers including chitosan, alginate, cellulose, and carrageenan have been used to synthesize stable biopolymeric electrolytes with improved electrical and mechanical properties. Among this biopolymer algae(carrageenan) based biopolymer was chosen as the host polymer which are extracted from red seaweed species. Iota carrageenan is a kind of carrageenan. The electrolyte prepared by Iota carrageenan has maximum conductivity as 3.86×10^{-6} Scm^{-1} at room temperature.

But the prepared pure iota carrageenan film shows fungal activity within 5 days (Figure 1). To overcome this issue, a blend technique is used. For blending, the gum based biopolymer, acacia gum is selected. Different concentration of polymers have taken to prepare the blend polymer electrolyte. The prepared electrolyte is optimized in terms of conductivity. There is a slight improvement in the conductivity after blending. However, the fungal activity of pure Iota carrageenan is avoided. In order to improve the flexibility and the conductivity of the blend, plasticizers are added with the optimized blend.

Modern technology requires efficient and dependable energy storage technologies. To fulfill the need of the society, new electrolyte materials with higher conductivity have to be identified. So that lithium based salts are added with the plasticized polymer blend.

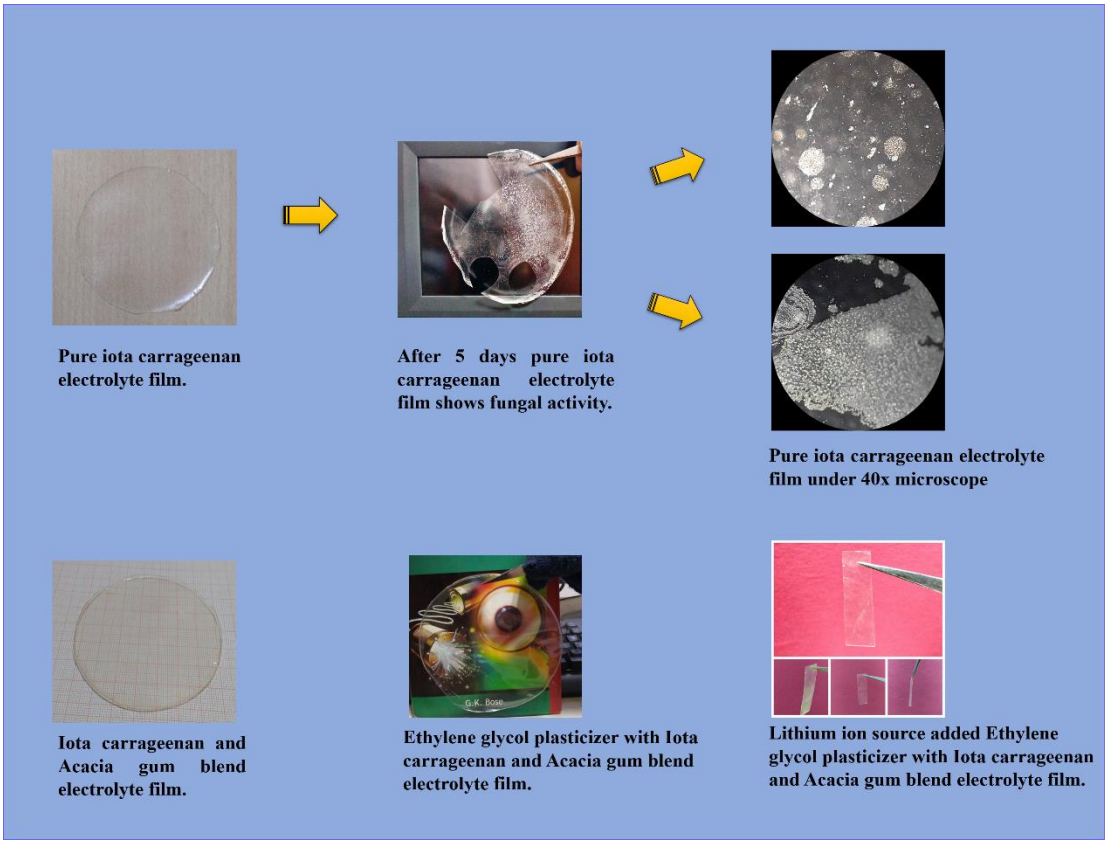
Pure iota carrageenan electrolyte film.
After 5 days pure iota carrageenan electrolyte film shows fungal activity.
Pure iota carrageenan electrolyte film under 40x microscope
Iota carrageenan and Acacia gum blend electrolyte film.
Ethylene glycol plasticizer with Iota carrageenan and Acacia gum blend electrolyte film.
Lithium ion source added Ethylene glycol plasticizer with Iota carrageenan and Acacia gum blend electrolyte film.

Figure 1 Research problem while preparing the biopolymer-based electrolyte.

5. Organization of Thesis

The research problem mentioned earlier have been thoroughly explored and defined through the utilization of a range of analytical methods. The study's endeavors are succinctly outlined in Figure 2, encapsulating the various characterization activities conducted within this research.

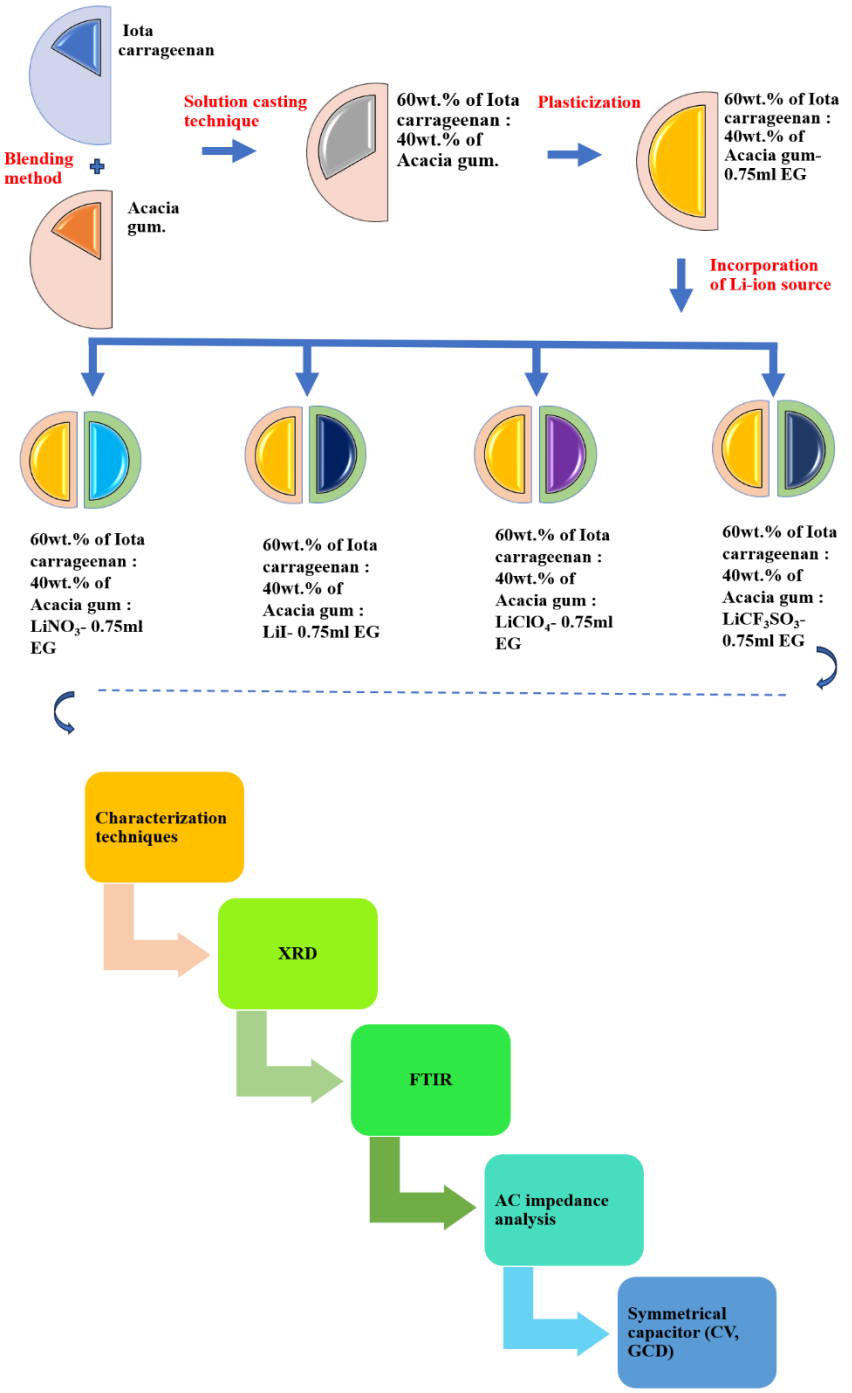
Iota carrageenan
Blending method
Acacia gum.
Solution casting technique
60wt.% of Iota carrageenan : 40wt.% of Acacia gum.
Plasticization
60wt.% of Iota carrageenan : 40wt.% of Acacia gum- 0.75ml EG
Incorporation of Li-ion source
60wt.% of Iota carrageenan : 40wt.% of Acacia gum : $LiNO_3$- 0.75ml EG
60wt.% of Iota carrageenan : 40wt.% of Acacia gum : LiI- 0.75ml EG
60wt.% of Iota carrageenan : 40wt.% of Acacia gum : $LiClO_4$- 0.75ml EG
60wt.% of Iota carrageenan : 40wt.% of Acacia gum : $LiCF_3SO_3$- 0.75ml EG
Characterization techniques
XRD
FTIR
AC impedance analysis
Symmetrical capacitor (CV, GCD)

Figure 2 Outline of thesis research work

The thesis is organized according to the following outlined contents:

Chapter 1 This section explores the needs of energy storage systems, as well as groundbreaking resources and their various types, such as batteries, capacitors, supercapacitors, and fuel cells. Types of supercapacitors based on electrode materials are symmetrical and asymmetrical capacitors. The fundamentals about electrodes and

electrolytes is explained. The electrolyte used in a supercapacitor plays a crucial role in its overall performance and characteristics. The electrolyte serves as a medium for ion conduction and allows the movement of ions between the electrodes, enabling the storage and release of electrical energy. The merit of solid biopolymer electrolytes has advantages such as easy preparation, purity, long-term stability, structure, and flexibility are discussed.

Chapter 2 This section reviews the current literature on biopolymer electrolytes utilized for electrochemical applications. Mainly, carrageenan and gum-based polymer electrolytes are taken for review. The aim is to identify any research gaps and areas of interest for further investigation. The review of biopolymer blend with lithium salt added electrolytes are identified and discussed for the subject of the study. The fabrication of electrochemical devices using the electrolytes are discussed .The properties of the device ~~is~~ are analyzed in terms of specific capacitance, energy density, and power density.

Chapter 3 presents the materials chosen for the synthesis of plasticized biopolymer electrolytes. The various preparation methods for the preparation polymer electrolytes such as spin coating technique, phase inversion technique, and solution casting technique are analyzed. This chapter also explains about the methods to improve the conductivity of the polymer electrolytes. The techniques involved in the characterization of polymer electrolytes such as X-ray diffraction (XRD), Fourier transform infrared (FTIR, AC impedance studies, Ion transport measurements and Electrochemical analysis are discussed. This chapter also discusses the process behind the aforementioned characterization.

Chapter 4 presents the optimization of the biopolymer blend. The blend comprising of Iota carrageenan (IC) and Acacia gum (AG) based biopolymer electrolytes are prepared by solution casting method. X-ray diffraction studies are used to investigate the amorphous nature of bio polymer blend electrolyte. The functional groups and the formation of complexes between polymer chains and plasticizer are identified by Fourier transform infrared analysis. The dielectric behavior is measured by using an AC impedance analyzer at various temperatures (303–373 K) and frequencies (1 Hz – 1 MHz). The prepared electrolyte are characterized by XRD, FTIR and AC impedance analysis to identify the higher conducting polymer electrolyte. To increase the

flexibility and the conductivity of the blend, various percentages of Ethylene glycol (EG) is added to prepare plasticized polymer blend electrolytes. For 0.75ml of EG added electrolyte, the highest conductivity of 2.96×10^{-4} $Scm^{-1}$is obtained. The Arrhenius behavior is analyzed to identify the temperature dependence of conductivity of polymer electrolyte films. The minimum activation energy of 0.06 eV is found for 0.75ml EG added sample. The tangent analysis is used to determine relaxation time (τ). The non-Debye character of the electrolytes is analyzed by the dielectric and modulus spectra.

Chapter 5 discusses about the Solid-state polymer electrolyte system prepared by Iota carrageenan /Acacia gum / ethylene glycol / Lithium nitrate ($LiNO_3$) using the solution cast technique. The structural characterization has done by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analysis. The electrolyte with 30 wt. % $LiNO_3$ incorporated blend polymer (IAN30) has the higher conductivity as 1.77×10^{-3} Scm^{-1}, activation energy as 0.02eV and ion transport number as 0.999. The non-Debye property of polymer electrolytes is confirmed by studies on the frequency dependence of dielectric and modulus spectra. IAN30 is used for the fabrication of symmetrical capacitor. There are no redox peaks in the Cyclic voltammetry (CV) response through its entire potential range for EDLC behavior. From the galvanostatic charge/discharge (GCD) studies of prepared symmetrical supercapacitor, discharge time and specific capacitance (C_s) values are calculated as 16s and 22 F/g respectively.

Chapter 6 explains the Solid polymer electrolyte developed by using the optimized blend of iota carrageenan / Acacia gum / ethylene glycol / Lithium iodide (LiI) using the solution cast technique. The amorphous nature and the presents of functional group in the electrolyte are characterized using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analysis respectively. The conductivity of the blend electrolytes has measured by using an impedance analyzer. Among them, the one with 15 wt. % LiI incorporated polymer electrolyte (referred to as IAI15) exhibits the higher conductivity as 1.21×10^{-3} Scm^{-1}. It also has low activation energy of 0.05 eV and a high ionic transport number of 0.999. The frequency dependence of the dielectric parameters and the dielectric loss tangent is used to confirm the non-Debye property of the prepared polymer electrolytes. Furthermore, the specific electrolyte (IAI15) is utilized in the fabrication of a symmetric capacitor. Remarkably, the cyclic

voltammetry (CV) response shows no redox peaks across its entire potential range, indicating Electric double-layer capacitor (EDLC) behavior. Through galvanostatic charge/discharge (GCD) studies on a prepared symmetrical capacitor, the discharge time and specific capacitance (C_s) values are determined as 30s and 150F/g respectively.

Chapter 7 presents lithium-ion conducting solid polymer electrolytes is prepared through iota carrageenan / Acacia gum / ethylene glycol / lithium triflate ($LiCF_3SO_3$) using the solution casting method. The improvement in amorphous nature and molecular complexations of the resulting electrolytes are analyzed through X-ray diffraction (XRD) and Fourier transform infrared analysis (FTIR). AC impedance analysis spectra demonstrate that the addition of 50 wt. % of $LiCF_3SO_3$ salt into the polymer electrolyte blend (IATF50) results in higher ionic conductivity of 3.18×10^{-3} S/cm, and activation energy of 0.03 eV. The dielectric and modulus spectra further confirms the non-Debye nature of the electrolyte. From the Transference Number measurement, it is confirmed that the conductivity is mostly occurred due to Li ions and IATF50 sample is chosen for the fabrication of a Symmetrical supercapacitor. Galvanostatic charge/discharge studies shows the discharge characteristics with a duration of 30s and a specific capacitance (C_s) value of 100 F/g.

Chapter 8 discussed the lithium-ion conducting Solid Polymer Electrolytes are synthesized by iota carrageenan / Acacia gum / ethylene glycol / lithium perchlorate ($LiClO_4$) - (IAO15) by solution casting method. The X-ray diffraction (XRD) and Fourier transform infrared analysis (FTIR) are used to analyze the structural and molecular complexation. AC impedance analysis spectra show that the incorporation of 15 wt. % of $LiClO_4$ salt into a blend polymer electrolyte (IAO15) shows the ionic conductivity of 2.02×10^{-2} S/cm and activation energy (0.022 eV). The dielectric and modulus spectra confirm the non-Debye nature of the sample. From the Transference Number Measurement, it is observed that the conductivity is due to Li ions and IAO15 sample is chosen for the fabrication of a Symmetrical supercapacitor. At 3.6 Ag^{-1} current density, the power and energy densities are noted as 7452 Wkg^{-1} and 165.6 $Whkg^{-1}$ respectively.

Chapter 9 explains summary and conclusion of the carried-out research in this thesis. The biopolymer-based electrolytes are synthesised by solution casting technique. The optimized blend biopolymer electrolyte comprising of by Iota carrageenan /Acacia gum attains a conductivity as 4.77×10^{-6} Scm^{-1} and the plasticized blend polymer shows ionic conductivity as 2.96×10^{-4} Scm^{-1}. The ionic conductivity is further improved by the addition of different lithium salts ($LiNO_3$, LiI, $LiCF_3SO_3$ and $LiClO_4$) with the higher conducting plasticized blend. In terms of conductivity, $LiClO_4$ added electrolyte attains a higher conductivity as 2.02×10^{-2} S/cm. A supercapacitor is fabricated by using the higher conductivity polymer electrolyte attained from each Li added system. The specific capacitance, Energy density, Power density are calculated. From the above mentioned, the supercapacitor fabricated by using $LiClO_4$ incorporated polymer blend electrolyte shows the higher power density, energy density as 7452W/Kg,166Wh/Kg compared with the other. Compared with the previous work, it attains exceptional electrochemical performance in terms of power and energy density. So that it is concluded that the prepared lithium incorporated biopolymer plasticized blend is suitable for supercapcitor applications.

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List of publications

1) **M. Nandhinilakshmi**, D. Vanitha, N. Nallamuthu, K. Sundaramahalingam, P. Saranya "Investigation on conductivity and optical properties for blend electrolytes based on iota carrageenan and acacia gum with ethylene glycol", journal of materials science: materials in electronics. **Impact factor 2.77.**
2) **M. Nandhinilakshmi**, D. Vanitha, N. Nallamuthu, K. Sundaramahalingam, P. Saranya "Fabrication of Symmetric Super Capacitor Using Lithium - ion Conducting IOTA Carrageenan - Based Biopolymer Electrolytes", Journal of Polymers and the Environment. **Impact factor 5.3.**
3) **M. Nandhinilakshmi**, D. Vanitha, N. Nallamuthu, K. Sundaramahalingam, P. Saranya, A. Shameem "Fabrication of high - performance symmetrical supercapacitor using lithium iodide - based biopolymer electrolyte", Ionics. **Impact factor 2.96.**